

REACTIVE ABSORPTION OF H₂S BY A SOLUTION OF SO₂ IN POLYGLYCOL ETHER

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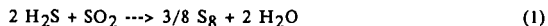
Keywords: Absorption with Reaction, Mass Transfer with Reaction, Plate Efficiency

INTRODUCTION

When coal is gasified, most of the total sulfur content is converted to hydrogen sulfide (H₂S) or, to a lesser extent, carbonyl sulfide (COS). The H₂S concentration in the coal gas depends on the amount of sulfur initially present in the coal and on the nature of the coal-gasification process used. Gas-phase concentrations are typically several thousand ppm H₂S. Because of environmental restrictions and process requirements, H₂S must be removed from coal-derived gas streams.

The required degree of H₂S removal depends on use of the gas. In some cases, selective absorption of H₂S is desirable. In other cases, co-absorption of CO₂ and light hydrocarbons allows these components to be recovered as separate products. To meet this wide range of processing requirements, the U. C. Berkeley Sulfur Recovery Process (UCBSRP) is being developed as a less-costly alternative to conventional sulfur-recovery technology [1]. The reactive absorption of H₂S by a polyglycol ether solution of SO₂ is but one step in this process.

The UCBSRP (Figure 1) consists of six basic steps. First, H₂S is absorbed in the primary absorber by a polyglycol ether (Diethylene glycol methyl ether or DGM). Second, by mixing the H₂S-rich solvent with a slight excess of SO₂ dissolved in the same solvent, all the H₂S can be reacted away to form sulfur by the following irreversible, liquid-phase reaction:



Only a small portion of the absorbed H₂S reacts in the primary absorber; most reacts in the reactor/crystallizers. Third, the dissolved sulfur formed by the reaction is crystallized and separated from the solvent in the reactor/crystallizers. Fourth, the water of reaction and any residual dissolved gases must be stripped from the solvent in the solvent stripper. Fifth, a portion of the recovered, marketable sulfur product is burned with exactly stoichiometric air in the furnace. The heat of combustion of sulfur is recovered in a waste-heat boiler and provides an energy credit for the process. Finally, the SO₂ produced by combustion is absorbed by the cool, lean solvent from the solvent stripper to provide the SO₂-rich solvent stream used in step two.

The key to this process is the irreversible, liquid-phase Claus reaction, equation 1. This reaction, even when carried out at temperatures below 100°C, proceeds rapidly to completion in the presence of an appropriate homogeneous liquid-phase catalyst (3-pyridyl carbinol). By this reaction the large H₂S stripping costs associated with most conventional technologies are avoided, and the cooled H₂S-free solvent from the crystallizer can be recycled back to the primary absorber without further processing. Because the solvent that is fed to the primary absorber is free of H₂S, the treated gas can easily meet a 1-ppm-or-less outlet specification.

Design of both the primary absorber and the SO₂ absorber requires knowing the tray efficiencies. Sieve-tray efficiencies for physical absorption of H₂S and SO₂ were determined at atmospheric pressure. The main solvent feed to the primary absorber contains a small amount of SO₂ that reacts with the H₂S being absorbed on the upper trays. Chemical reaction in the liquid phase can enhance the rate of mass transfer of a gas that is being absorbed. The effect that the simultaneous chemical reaction has on H₂S absorption rates, and thereby tray efficiencies, was studied both by modelling and by experimentation. Tray-efficiency correlations from the literature were used to correlate the experimental data and to predict the high-pressure tray efficiencies that are necessary for designing the high-pressure primary absorber.

TRAY-EFFICIENCY MODELS

One of the most readily available and widely used procedures for estimating tray efficiencies is the procedure developed in the late 1950's by the American Institute of Chemical Engineers (AIChE). This procedure uses mass-transfer correlations first to predict the point efficiency and then to convert the point efficiency to a Murphree tray efficiency. Chan and Fair [2] followed the basic AIChE design strategy but used more current mass-transfer correlations to improve the accuracy of sieve-tray efficiency predictions. The basic procedure, without presenting the correlations, begins with defining the point efficiency, E_{OV} , as

$$E_{OV} = (y_{in} - y) / (y_{in} - y^*) \quad (2)$$

where

$$y^* = m x_{loc} \quad (3)$$

The inlet and outlet gas compositions to and from the element of solvent are y_{in} and y respectively; y^* is the gas composition that would be in equilibrium with x_{loc} , the uniform composition of the solvent at the location of interest on the tray. The slope of the equilibrium line is m . A more useful equation for estimating the point efficiency has been derived by analyzing the mass-transfer process by using the addition-of-resistances theory along with the assumption that the gas moves upward, in plug flow, through a well-mixed liquid. The results of the derivation are

$$E_{OV} = 1 - \exp(-N_{OV}) \quad (4)$$

where N_{OV} is the number of mass-transfer units based on the overall gas-phase mass-transfer driving force. The overall number of transfer units is related to number of transfer units based on the mass-transfer driving forces of the individual phases by

$$N_{OV} = [1 / N_v + \lambda / N_L]^{-1} \quad (5)$$

where

$$N_v = k_v a_i t_v \quad (6)$$

$$N_L = k_L a_i t_L \quad (7)$$

$$\lambda = (m V) / L \quad (8)$$

If the individual gas- and liquid-phase mass-transfer coefficients, $k_v a_i$ and $k_L a_i$, and their respective contact times, t_v and t_L , are known or can be estimated reasonably by correlations, the number of gas- and liquid-phase mass-transfer units, N_v and N_L , can be determined. To calculate N_{OV} by equation 5, one needs to know λ , the ratio of the slope of the equilibrium line, m , to the slope of the operating line, L/V . The point efficiency is then calculated by equation 4. It still remains to convert the point efficiency to a Murphree tray efficiency.

Murphree vapor tray efficiency, E_{mv} , as defined by equations 9 and 10 below, is a measure of how closely the change in gas composition across a tray approaches the composition change that would occur if the gas were to leave the tray in equilibrium with the liquid exiting the tray. The gas streams above and below the tray are assumed to be perfectly mixed.

$$E_{mv} = (y_{in} - y_{out}) / (y_{in} - y^*) \quad (9)$$

where

$$y^* = m x_{out} \quad (10)$$

The equilibrium backpressure of the absorbed gas, y^* , for the Murphree vapor tray efficiency is based on the concentration of dissolved gas in the solvent at the tray outlet, x_{out} , whereas the point efficiency is based on local solvent concentration, x_{loc} , which may be changing as the solvent flows across the tray. By using an eddy-diffusion model for crosscurrent flow to describe liquid mixing on the tray, and by assuming that the inlet gas is perfectly mixed, the two efficiencies can be related to each other through λ and the dimensionless Peclet number, Pe .

$$Pe = Z_L^2 / (D_e t_L) \quad (11)$$

The length of the liquid flow path, Z_L , is the distance between the inlet and outlet weirs on the

tray. The eddy diffusivity, D_e , can be calculated from correlations.

Two limiting regimes are encountered. For complete mixing of the solvent on the tray, corresponding to Pe equal to zero, E_{mv} is equal to E_{ov} . When the solvent flows across the tray in plug flow, corresponding to Pe equal to infinity, the maximum improvement of E_{mv} over E_{ov} is obtained. The Peclet number for the tray and operating conditions used in the present study is approximately equal to 0.01. This low value of Pe indicates that the solvent on the tray is well-mixed and that the measured Murphree efficiencies are equivalent to point efficiencies.

TRAY EFFICIENCY FOR ABSORPTION WITH CHEMICAL REACTION

If absorption with chemical reaction is occurring, the liquid-phase mass-transfer coefficient may increase relative to the coefficient for strictly physical absorption due to the reaction depleting the concentration of the absorbed gas near the gas-liquid interface. To obtain this enhancement, a significant portion of the reaction must occur in the liquid diffusion film near the gas-liquid interface rather than in the bulk solvent. When this is the case, $k_L a_i$ for physical absorption should be multiplied by an enhancement factor, $\phi \geq 1$, to obtain the liquid-phase mass-transfer coefficient for reactive absorption, $k_L^* a_i$, which is then used in equation 7 to obtain N_L .

$$k_L^* a_i = \phi k_L a_i \quad (12)$$

To find ϕ , an appropriate mass-transfer model, such as the film model or the Higbie penetration model must be chosen. The reaction regime (slow, fast, or instantaneous), the order of the reaction, and the reaction equilibrium (reversible or irreversible) must be determined. Then a value for the enhancement factor may be obtained from one of the well-known solutions to the differential equations that describe absorption with chemical reaction under these models [3].

If the tray is well-mixed ($Pe = 0$) the calculation of E_{mv} is straightforward. However, a more rigorous treatment [4] is required when the enhancement factor is a function of one or more of the reactant concentrations and these concentrations vary along the liquid-flow path on the tray. In this case the point efficiency will vary with concentration across the tray and will complicate the calculation of E_{mv} .

In determining efficiencies, the correct value of y^* to use in equations 2 or 9 depends on the reaction rate. For *very fast* reactions, in which most of the absorbed gas reacts in the film and never makes it to the bulk solvent, y^* is equal to zero. For *slow* reactions very little reaction occurs in the diffusion film. Most of the absorbed gas passes into the bulk liquid where it slowly reacts, and y^* should properly reflect the actual concentration of absorbed gas in the bulk liquid. This presents a problem if one desires to determine E_{mv} since it would require an *in situ* method of measuring the concentration of dissolved gas right at the tray outlet to calculate y^* . However, in the case of *slow* reactions, because very little reaction is occurring in the liquid film near the interface, no mass-transfer enhancement is expected, and the tray efficiency for absorption with slow reaction should be equal to the tray efficiency for physical absorption. The system under investigation falls within the *slow* reaction regime.

REACTION IN THE BULK LIQUID ON THE TRAY

In a well-mixed flow absorber operating at steady-state, as for example a sieve-tray absorber, the concentrations of dissolved gas (A) and reactant (B) are uniform throughout the bulk liquid on the tray and remain constant over time. The absorber can then be modeled as a continuously-stirred-tank reactor (CSTR). The design equation for a sieve tray acting as a CSTR/absorber requires the flow of dissolved component A in the liquid being fed to the tray plus the rate of absorption of A from the gas to be equal to the flow of dissolved, unreacted A that leaves the tray plus the rate at which A is consumed by reaction while the liquid is on the tray. For the irreversible, second-order reaction between A and B



with a reaction rate of

$$\text{Rate} = k_2 C_{Ao} C_{Bo} \quad (14)$$

the CSTR/tray design equations is

$$Ra_i = \phi k_L a_i (C_{Ai} - C_{Ao}) = (C_{Ao} - C_{Ain})/\tau + k_2 C_{Ao} C_{Bo} \quad (15)$$

The concentration of dissolved A at the interface and in the bulk solution are C_{Ai} and C_{Ao} respectively. The residence time (Q_L/H_L) of the liquid in the tray is τ , where Q_L is the volumetric flow of liquid to and from the tray and H_L is the hold-up (volume) of liquid on the tray. The second-order reaction-rate constant is k_2 , and Ra_i is the rate of absorption per unit volume.

A *slow* reaction is one for which the reaction term is not negligible although the enhancement factor is still equal to one. For the enhancement factor to be one while substantial reaction is occurring in the bulk solution, the condition that the rate of reaction in the film is much less than the rate of absorption must be satisfied [3]. This condition requires that

$$M = D_{LA} k_2 C_{Bo}/k_L^2 \ll 1 \quad (16)$$

When condition 16 is met, the tray efficiency will remain unchanged from the efficiency for physical absorption even though the rate of reaction in the bulk liquid on the tray is appreciable. The rate of absorption, however, will be greatly improved because the reaction reduces the concentration of component A in the bulk solution (C_{Ao}), thus improving the driving force for mass transfer. When operating within this regime, the reaction rate constant, k_2 , can be calculated from equation 15 if the rate of absorption and the concentrations of A and B are known.

Hydrogen sulfide absorption by solutions of SO_2 is a case of absorption with irreversible, second-order chemical reaction containing a volatile dissolved reactant. Both penetration-model and film-model analyses indicate that condition 16 is met and that the reaction is too slow to cause an enhancement of the liquid-phase mass-transfer coefficient [5]. The reaction, then, occurs predominately in the bulk liquid, and the tray efficiency for reactive absorption should be equal to the efficiency for physical absorption.

PHYSICAL ABSORPTION OF H_2S AND SO_2

Murphree vapor tray efficiencies for physical absorption of H_2S and SO_2 were determined with an apparatus which consisted of a single 0.10-meter (4-inch) sieve tray with 4% free area placed in a circulating gas stream. Solvent was fed to the tray continuously, on a once-through basis. With this apparatus H_2S and SO_2 gas feed rates, gas- and liquid-phase compositions and temperatures, and total gas and liquid flows were measured to determine absorption rates and tray efficiencies. For physical absorption the solvent feed was free of dissolved gas.

Tray efficiencies were determined for physical absorption of SO_2 over an inlet gas concentration range of 400 to 4500 ppm. The liquid and gas flows were constant at 3.55 mole/min (6.97 cm³/s) and 8.57 mole/min (0.427 m³/m²-s) respectively. The total pressure was 122 kPa. The average efficiency for this system was 0.59 ± 0.11 .

Tray efficiencies for physical absorption of H_2S by DGM were determined at 30°C and 40°C for the same total pressure and solvent and vapor flows as above. The inlet gas concentration range was 1200 to 2700 ppm. The H_2S tray efficiencies at 40°C averaged 0.16 ± 0.09 and those at 30°C averaged 0.18 ± 0.08 . These efficiencies are quite a bit lower than the SO_2 efficiencies because of the much lower solubility of H_2S in DGM. Sulfur dioxide is more than ten times as soluble in DGM as is H_2S . The slope of the equilibrium line, m , increases with decreasing gas solubility. For gas absorption under liquid-phase control (which is the case for this system) $\lambda/N_L \gg 1/N_V$. When this is the case, $N_{OV} \approx N_L/\lambda$. Therefore, if m increases due to lower gas solubility, λ must increase in proportion and N_{OV} must decrease, which results in a lower value calculated for E_{OV} . The efficiency for H_2S at 30°C is slightly higher than the efficiency for H_2S at 40°C because of the increased H_2S solubility in DGM at the lower temperature, although the increase in tray efficiency is less than the uncertainty of the efficiency measurements.

Table I compares the measured tray efficiencies for H_2S and SO_2 at various operating conditions to the predictions of the Chan and Fair model [2]. The average absolute error of the tray-efficiency predictions is 9%. This very good agreement with the measured efficiencies provides encouragement for using the model to provide high-pressure tray efficiencies.

HYDROGEN SULFIDE ABSORPTION WITH CHEMICAL REACTION

A. Calculations

Hydrogen sulfide absorption rates were also measured for the case when H_2S is absorbed and undergoes chemical reaction with SO_2 dissolved in the solvent. All the reactive-absorption experiments were with excess SO_2 (from about 2 to 7 times the stoichiometric equivalent). A homogeneous catalyst, 3-pyridyl carbinol (3-PC), was dissolved in the solvent, DGM, to increase the reaction rate. The catalyzed, irreversible, liquid-phase reaction between H_2S and SO_2 was found to be first-order in both reactants by Neumann [6] and Crean [7]. Both Neumann and Crean found that the following rate expression fit their kinetic data.

$$\text{Rate} = k_2 [H_2S] [SO_2] \quad (17)$$

In the present study the rate expression of equation 17 was used in conjunction with the CSTR/tray design equation (eqn. 15) and the reactive-absorption rate data to calculate second-order rate constants at various catalyst concentrations, temperatures, and H_2S feed rates. If the solvent feed to the tray contains no dissolved H_2S , as was the case for all the reactive-absorption experiments, the rate of H_2S absorption ($R_{A1}H_L$) must equal the rate at which dissolved H_2S leaves the tray in the exiting solvent plus the rate at which H_2S is consumed by reaction on the tray. Equation 15 becomes

$$R_{A1}H_L \text{ (moles } H_2S/\text{sec)} = Q_L [H_2S]_{out} + k_2 H_L [H_2S]_{out} [SO_2]_{out} \quad (18)$$

Use of this equation requires knowledge of the concentrations of dissolved reactants on the tray. Because concentrations could not be measured *in situ*, the concentration of H_2S on the tray was calculated from the tray efficiency for H_2S . If the inlet concentration of SO_2 is known, the concentration of SO_2 leaving the tray can be determined by mass balance. Since the rate of H_2S absorption, tray hold-up, and solvent flow to the tray are measured quantities, equation 18 can be solved for the reaction-rate constant, k_2 .

B. Reactive-Absorption Results

1. Verification of Reaction-Rate Constant

Reactive-absorption rate data were collected at various temperatures, catalyst concentrations, and H_2S feed rates. The concentration of dissolved SO_2 in the solvent feed to the tray was approximately 0.001 m.f. for all the reactive-absorption experiments, and the liquid and gas flows were constant at 3.55 mole/min (6.97 cm^3/s) and 8.57 mole/min (0.427 m^3/m^2-s) respectively. At each catalyst concentration and temperature combination, two absorption runs were done for an H_2S feed rate of approximately 13.0 standard cubic centimeters per minute and two runs were performed with the H_2S feed rate set to achieve an tray-inlet gas concentration of approximately 1900 ppm. For each run the second-order rate constant was calculated by the procedure described above. The first set of reactive-absorption experiments, at a catalyst concentration of 0.015 M 3-PC and a tray temperature of 40°C, returned an average second-order rate constant of 11.2 liter/(mole-s). This value compares fairly well to the rate constant of 32 liter/(mole-s) that was measured at the same catalyst concentration by Neumann [6], who used an adiabatic batch reactor. Extrapolating Crean's data to 0.015 M 3-PC gives a second-order rate constant of 20 liter/(mole-s). Crean's measurements were taken using a stop-flow apparatus connected to a UV-spectrophotometer. This fair agreement among data collected by very different techniques suggests that the method of calculating reaction-rate constants from the reactive-absorption data is valid.

2. Effect of 3-PC Concentration on Reaction-Rate Constant

Figure 2 shows the effect of catalyst concentration on the rate constant at 40°C. The second-order rate constants range from about 10 liter/(mole-s) at 0.015 M 3-PC to about 80 liter/(mole-s) at 0.030M 3-PC. The large error bars result from the uncertainty in the assumed tray efficiency.

The relationship between rate constant and catalyst concentration is fairly linear as was found by Crean and Neumann; however, the negative intercept does not agree with the intercept

through the origin which Crean's data gave. Crean also found a linear dependence of k_2 on catalyst concentration (eqn. 22), whereas this study found a higher order dependency.

$$k_2 = k_3 [3\text{-PC}]_0 \quad (22)$$

where the third-order rate constant, k_3 , does not vary with catalyst concentration. One possible mechanism that would fit this rate expression, although not confirmed, is that H_2S and 3-PC react rapidly and are in equilibrium with the complex they form. The H_2S -catalyst complex then reacts with SO_2 in the rate-limiting step to form a second complex which reacts very rapidly with a physically dissolved H_2S molecule to form sulfur and water. Crean's data are, at least, consistent with this mechanism. Even though a proven reaction mechanism has not been found, the rate expression of equation 17 fits the data fairly well and is simple enough to use easily in numerical calculations.

3. Effect of Reaction on H_2S Absorption

Figure 3 shows the relationship between H_2S absorption rate and reaction-rate constant at an assumed tray efficiency of 0.16. These data were taken at a tray-inlet gas-phase concentration of H_2S of 1900 ppm. Even though the reaction is too slow to cause any enhancement in the liquid-phase mass-transfer coefficient, the reaction does provide significant improvement in the absorption rate of H_2S . It accomplishes this by lowering the bulk liquid-phase concentration of H_2S , which results in a greater overall mass-transfer driving force between the gas and the bulk liquid. This same effect could be achieved in physical absorption by increasing the liquid flow rate to the level that is necessary to achieve the same low concentration of H_2S in the bulk liquid. For example, to achieve the same rate of absorption without reaction that was measured for reactive absorption with a rate constant near 10 liter/(mole-s), the liquid flow would have to be increased by a factor of 2.4. The curve in the figure is from a simulation of a single sieve tray modeled as a CSTR and given the same feed conditions, liquid hold-up, and tray efficiency as the sieve tray in the apparatus. The complex between H_2S and 3-PC was also considered in the model. The two dashed curves represent the uncertainty in the assumed tray efficiency and provide upper and lower bounds for k_2 at a given absorption rate.

SUMMARY

The tray-efficiency model of Chan and Fair adequately predicts, to within about 10%, the measured physical-absorption tray efficiencies for H_2S and SO_2 at low pressure (122 kPa). These correlations will be used to predict tray efficiencies at the high pressures that will be used in designing the primary absorber of the UCBSRP.

A second-order rate expression (first-order in both reactants) and a CSTR-model for the sieve tray were used to calculate second-order rate constants from the reactive-absorption data for H_2S absorption on a sieve tray. The method gave rate constants that were in fair agreement with values that were determined in other studies [6, 7]. The rate constant increases steeply with catalyst concentration, and a rate constant of 100 liter/(mole-s) should be easily achievable at a low catalyst concentration (near 0.03 M). The reaction is too slow to cause enhancement of the liquid-phase mass-transfer coefficient; nevertheless, a substantial improvement in H_2S absorption rate occurs because the reaction lowers the bulk concentration of dissolved H_2S . This is the same effect as seen in physical absorption when the liquid flow rate is increased. Although the rate data that were collected in this study do not fit the proposed rate expression as well as the data of Neumann and Crean, the expression should be adequate for modeling and design of the primary absorber.

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Table 1: Comparison of Experimentally-Determined Tray Efficiencies to Predicted Efficiencies

($V=8.60$ mole/min, $P=122$ kPa)

Temp. °C	Liq. Flow mole/min	weir ht. cm	measured E_{mv}	predicted E_{mv}	error
SO₂					
40	1.62	1.91	0.50	0.48	- 4.0%
40	1.62	2.54	0.50	0.54	8.0%
40	3.55	2.54	0.59	0.54	- 8.5%
H₂S					
30	3.55	2.54	0.18	0.20	11.1%
40	3.55	2.54	0.16	0.18	12.5%
50	3.55	2.54	not determined	0.17	----

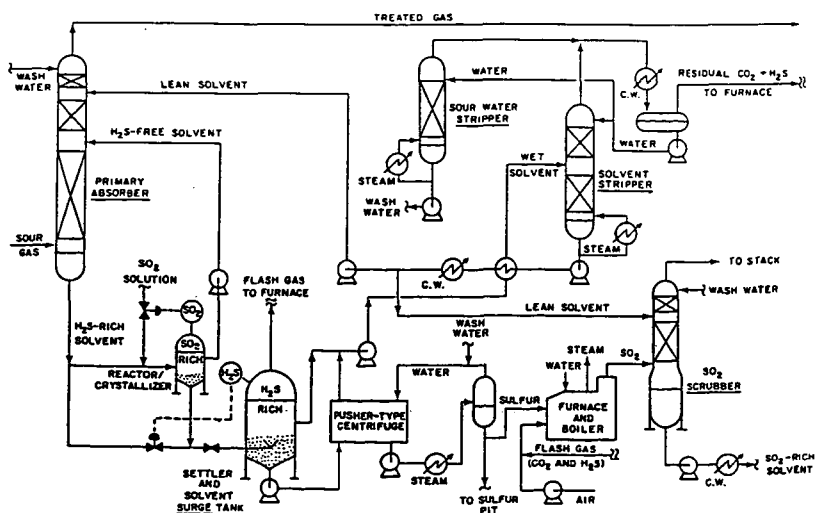


Figure 1: UCBSRP Configuration for High H₂S Selectivity

Figure 2: Effect of Catalyst Concentration on Reaction-Rate Constant

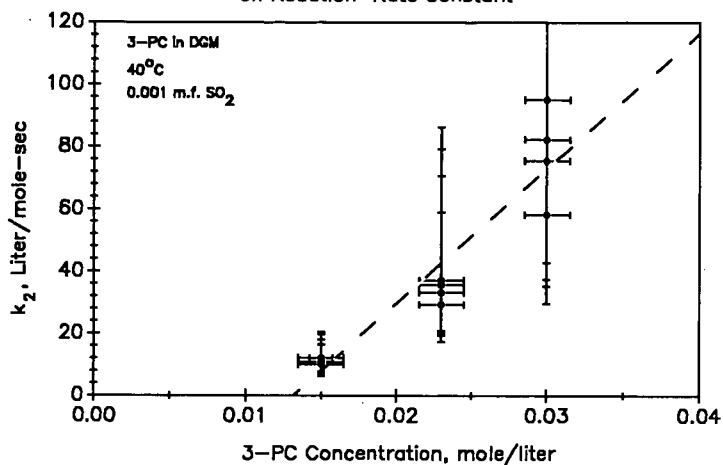


Figure 3: Effect of H₂S Absorption Rate and Assumed E_{mv} on Reaction Rate Constant

